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(54) Title: POLYMERS AND THEIR USES

## (57) Abstract

This invention relates to a copolymer having structural units derived from monomers which are (A) at least one ethylenically unsaturated alcohol, carboxylic acid or ester, with at least one of (B) an ethylenically unsaturated carboxylic ester with a polar group in the ester, and (C) an ethylenically unsaturated carboxylic amide. The invention also relates to the use of such a copolymer in hydrocarbon and aqueous fluid media.

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### POLYMERS AND THEIR USES

This invention relates to carboxylic polymers and their uses in aqueous media and hydrocarbon fluids.

Some of the physical properties of many hydrocarbon oils, such as crude oil, residual oils, diesel oil, lubricating oil or others boiling higher than gasoline are often unsatisfactory. Their viscosity may be too high for easy movement e.g. pumping under pressure or may show drag when being pumped under pressure, and or they have a tendency to deposit solids e.g. wax or asphaltenes. Hydrocarbon gases e.g. natural gas may also suffer from drag. Carboxylic polymers such as polymers of unsaturated esters e.g. alkyl (meth) acrylate esters are described for use as pour point depressants (to stop oil gelling with wax) or wax deposition inhibitors.

The flow characteristics of some aqueous media may also be unsatisfactory because their viscosity may be too high for easy movement, e.g. pumping or may have high drag, resulting from contact of liquid with the walls of pipes etc., especially under conditions of turbulent flow. Examples of such media are ones in the oil industry, in particular the exploration and production industry such as aqueous drilling fluids or muds well control fluid (to stop premature flow out from a well), and workover fluids (to maintain a well while remedial operations are performed downhole). In addition, examples of such media in public health include sewer liquids and storm drains, and water for fire hoses, and for medical purposes blood, plasma and aqueous saline.

Carboxylic polymers have now been discovered which can act to reduce drag (i.e. aiding pumping) or reduce asphaltene deposition (also increasing pumping rates), or reduce wax deposition.

According to a first aspect of the present invention, there is provided a

copolymer (including ter and higher polymers) having structural units derived from monomers which are (A) at least one ethylenically unsaturated alcohol, carboxylic acid or ester, with at least one of (B) an ethylenically unsaturated carboxylic ester with a polar group in the ester, and (C) an ethylenically unsaturated carboxylic amide. The copolymers may be derived from monomers A and/or B which are ethylenically unsaturated carboxylic acids or esters thereof, or esters of ethylenically unsaturated alcohols. The copolymers, may be acid esters, acid amides, mixed esters, ester amides or acid ester amides, or alcohol esters.

The present invention also provides a method of preparing the copolymers of the invention which comprises copolymerising the monomer A, with B and/or C, in particular, when monomer A is an ester, and especially when each of the monomers is derived from an ethylenically unsaturated carboxylic acid or ester or amide, or each is derived from an ester of ethylenically unsaturated alcohol.

The present invention also provides a method of preparing the copolymers of the invention which comprises reacting an ester polymer having structural units of A which is an ester of an ethylenically unsaturated carboxylic acid ( $A^1$ ), especially consisting essentially of such  $A^1$  units, with an hydroxy compound containing at least one additional polar group and/or with an organic primary or secondary amino compound with or without at least one additional polar group.

The present invention also provides a method of preparing the copolymers of the invention with structural units A, and B and/or C in which structural units  $A^1$  comprise carboxylic acids and optionally ester units, which comprises breaking an ester link in  $A^1$  e.g. by hydrolysing a corresponding copolymer of the invention in which structural units  $A^1$  are carboxylic esters especially ones without a polar side chain and especially of less than 6 carbon atoms in the alcohol part of the ester.

The present invention provides a method of preparing copolymers of the invention, which comprises reacting a polymer having structural units of  $A^{11}$  [which is at least one of an ethylenically unsaturated alcohol, an ester thereof and a mixture of ester units and units from said unsaturated alcohol  $A^{11}$  (but especially consisting essentially of such  $A^{11}$  units)] with a carboxylic acid (or derivative thereof especially an ester) containing at least one additional polar group. This reaction may be followed (if necessary or desired) by breaking ester links in structural units A.

The invention also provides complexes of the copolymers of the invention in which A is an ester monomer, and B and/or C contains a basic nitrogen atom

(hereafter copolymers D), with at least one acid in particular a carboxylic acid, which may be polymeric or of molecular weight less than 1000 e.g. less than 400. There are also provided complexes of the copolymers of the invention with structural units A<sup>1</sup> from carboxylic acid units alone or with ester units (copolymers E) with bases especially nitrogenous bases, which may be polymeric or of molecular weight less than 1000 e.g. less than 400. Preferably the complexes comprise the copolymers D and E.

5 The invention also provides a soluble concentrate with at least 10%, for example, at least 20% by weight of a copolymer or complex of the invention, in a solvent. The solvent may be an organic solvent for oil soluble copolymer and complexes. For water soluble copolymers or complexes, the solvent may be water. 10 The copolymer or complex may also be in a dispersion, with at least 10% e.g. at least 20% by weight of said copolymer or complex, the dispersion being in a liquid medium in which the copolymer is of reduced solubility or incompletely soluble. 15 For oil soluble copolymers or complexes, the medium is preferably aqueous while for water soluble ones the medium is preferably organic e.g. a hydrocarbon as described above.

The present invention also provides a hydrocarbon fluid e.g. a crude oil or residue oil or gaseous hydrocarbon which comprises at least one copolymer or 20 complex of the invention.

The present invention also provides a method of improving the flow of a fluid medium, which method comprises mixing with said fluid medium, a copolymer according to the present invention. The fluid medium may be aqueous-based, hydrocarbon-based or a multiphase medium comprising aqueous and 25 hydrocarbon components. Preferably, the fluid medium is moving, for example, along a confined path.

Thus, the present invention provides a method of improving the flow of a body of hydrocarbon fluid moving in a confined path (e.g. a constricted conduit such as a pipeline), which method comprises mixing with said body of hydrocarbon 30 fluid (before or while flowing) at least one copolymer or complex of the invention or concentrate or dispersion thereof, in particular an oil soluble one and especially one containing a copolymer of an ester A or a complex thereof, to increase the flow rate of said body by reducing drag in said body or avoiding a reduction in flow rate in said body due to formation of solids therein on cooling said body.

35 The present invention also provides a method of improving the flow of a

body of aqueous fluid (eg water) moving in a confined path e.g. a constricted conduit such as a pipeline which comprises mixing with said body of aqueous fluid (before or while flowing) at least one copolymer or complex as described above or concentrate or dispersion thereof, in particular a water-soluble one and especially one containing a copolymer of an acid A or alcohol A or a complex thereof, to increase the flow rate of said body by reducing drag in said body. The aqueous fluid usually contains more than 5% total soluble salts.

In the copolymers are structural units from at least one monomer A<sup>1</sup> which is preferably an ethylenically unsaturated acid or ester thereof or mixture of both.

The ethylenic unsaturated carboxylic acid for use, which may be monomer A<sup>1</sup>, may contain the unsaturated group alpha, beta or gamma, or in another location, to the carboxylic group. It may contain 3-17 e.g. 3-6 carbon atoms, and is especially an aliphatic alpha ethylenically unsaturated carboxylic acid of formula  $R^1CH=CR^2CO_2H$ , wherein each of R<sup>1</sup> and R<sup>2</sup> which may be the same or different is hydrogen or an alkyl group e.g. of 1-3 carbons, such as methyl, ethyl or propyl. Methacrylic and especially acrylic acids are preferred. The acid may be a mono, di or tricarboxylic acid, examples of the diacid being fumaric, maleic and crotonic acids.

The esters thereof for use as monomer A<sup>1</sup> may be from an aliphatic hydrocarbyl alcohol, with a short chain aliphatic group e.g. of 1-5 carbons and/or from a hydroxylic compound with a larger organic hydrocarbyl group such as of 6-40 e.g. 6-16 or 16-40 carbons. The alcohol or hydroxylic compound may have less than 50% molar (eg 1 - 30%, preferably, less than 20% and most preferably, 0.1 - 10%) groups with at least 6 carbons and is especially free of such groups.

In the ester each of the aliphatic and/or organic hydrocarbyl groups may be saturated or unsaturated, e.g. all saturated or all unsaturated, but preferably at least one e.g. the short chain one is saturated and the rest saturated or unsaturated.

The larger organic alcohol for use in the ester polymers may be aliphatic and preferably linear, but may be branched (e.g. with a branch methyl group). The alcohol may be saturated i.e. an alkanol in which case preferably at least 20% or 40% of the saturated aliphatic groups have 12-35 e.g. 15-35 carbons. The alcohol may be ethylenically unsaturated i.e. an alkenol in which case preferably at least 50% of the aliphatic groups in the copolymer have 12-35 e.g. 15-35 carbons and the molecular weight is at least 20,000 or 40,000. The alcohol may contain at least one unsaturated group e.g. 1-4 such as 1 or 2 or 3 or 4, especially 1

- unsaturated group. The unsaturated group may be beta, gamma, or in another location, to the alcohol group preferably non terminal and may be in a cis or trans configuration especially with any unsaturated groups non-conjugated. The aliphatic alcohol usually contains 14-40 carbons such as 15-25 carbons, especially 16, 18, 20, 22 or 24 carbons. The alcohol may be natural or synthetic e.g. from oxo or ALFOL processes. Examples of suitable alcohols are palmityl, hexadecyl, stearyl, octadecyl, eicosyl, docosyl, as well as oleyl alcohol and branched alcohols such as oxo alcohols e.g. 2-methyl eicosyl alcohol. The hydroxylic compound with the larger organic hydrocarbyl group may contain 6-16 carbons, e.g. with an alkyl group such as hexyl, octyl, isooctyl, 2-ethylhexyl, decyl, dodecyl, lauryl, tetradecyl or myristyl group. The larger organic hydrocarbyl group may be a cycloalkyl group e.g. of 5-7 carbon atoms such as cyclo-hexyl or cycloheptyl, cyclopentyl or an aromatic group of 6-12 carbons, such a phenyl, tolyl or xylyl, or aralkyl group e.g. of 7-13 carbons such as benzyl or 2-phenyl ethyl. The alcohols especially aliphatic ones saturated or unsaturated may be substantially pure, but are preferably mixtures of alcohols, e.g. as in tallow alcohol or mixtures of alkanols and/or alkenols of even carbon number, with one carbon number predominating with decreasing proportions of alkanols or alkenols of lower and higher carbon number (e.g. of Gaussian distribution) i.e. with carbon numbers distributed on either side of the major one. Such mixtures may contain at least 50% e.g. at least 80 or 90% (by mole) of one alkanol or alkenol. Examples of such mixtures are unsaturated alcohols e.g. of 16 or 18 carbon atoms containing in wt % 50-100% of cis-alkenol, and optionally 1-20% e.g. 5-20% of saturated alkanols, especially C14, C16 or C18 saturated alkanols (such as in commercial oleyl alcohol).
- Preferably the monomer A is an ethylenically unsaturated acid of 3-6 carbon atoms and/or an ester of an aliphatic hydrocarbyl alcohol with a short chain aliphatic group of 1-5 carbon atoms, and an ethylenically unsaturated acid of 3-6 carbon atoms. Especially preferred are acrylic or methacrylic acid and/or acrylates and methacrylates of methanol, ethanol or tert butanol.
- Thus monomer A may be of formula  $R^1CH=CR^2CO_2R^3$ , wherein each of  $R^1$ , and  $R^2$  which may be the same or different represents hydrogen or an aliphatic hydrocarbyl group e.g. an alkyl group of e.g. of 1-4 carbons such as methyl or ethyl and  $R^3$  may be as defined for  $R^1$  or  $R^2$  or represents a hydrocarbyl group of at least 6 carbons such as an alkyl or alkenyl group or other group e.g. as described for the larger hydrocarbyl group in the hydroxylic compound above. Preferably  $R^1$

is hydrogen and  $R^2$  is hydrogen alkenyl or alkyl, especially hydrogen or methyl and  $R^3$  is hydrogen, alkyl or alkenyl, cycloalkyl, aryl or aralkyl. In Monomer A,  $R^3$  can consist essentially of hydrogen or hydrocarbyl or comprises a mixture of monomers  $A^1$ , in which  $R^3$  as hydrogen and  $R^3$  as hydrocarbyl may be present, the ratio being  
 5 0.5-99.5:99.5-0.5, such as 0.5-50:99.5-50 or 99.5-50:0.5-50, e.g. 10-40:90-60, 5-40:95-60, 90-60:10-40, or 95-60:5-40.

A mixture of structural units for monomers  $A^1$  may be present with  $R^3$  hydrocarbyl, in particular ones with short chain alkyl for  $R^3$  and larger hydrocarbyl e.g. longer chain alkyl for  $R^3$  (e.g. so the longer chain aliphatic alcohol described  
 10 above is of formula  $R^3OH$ ). The molar ratio of monomers with such short to long chain group may be 0.5-99.5:99.5-0.5, in particular 10-90:90-10 especially 10-40:90-60. Increasing ratios of the longer chain monomer units tend to increase the hydrocarbon solubility of the copolymers, as well as their molecular weight. The molar ratio of monomers with  $R^3$  as short chain to  $R^3$  as larger e.g. long chain may  
 15 be 0.1-5:1:0.1-5 in particular 0.1-1:1:1-5, especially for oil soluble polymers and 1-5:1:0.1-1 for water soluble ones. Preferably, the long chain groups and especially all hydrocarbyl groups for  $R^3$  are absent so unit A especially consists essentially of unsaturated acid units.

Monomers A with groups  $R^3$  as an aliphatic group of 8 or more e.g. 14 or  
 20 more carbons may be substantially absent, or may be present so long as less than 30% e.g. 1-25%, 5-25% (or 5-15%) of the total aliphatic groups for  $R^3$  in the monomers A have 6-35 or 12-35 or 15-35 carbons or may be present with an average total aliphatic side chain for  $R^3$  of less than 12 carbons e.g. 1-11.9 such as 1-3.5, 1-2.5 or 4-8.

In the copolymers may also be structural units from at least one monomer B, which is an ester of an ethylenically unsaturated carboxylic acid and an organic mono hydroxy compound with at least one additional polar group ( $B^1$ ). The acid may be as described with respect to monomer A. The additional polar group may contain an oxygen, nitrogen or sulphur atom, especially one or more O and/or N  
 25 atoms. The or each polar group may be a side chain substituent on a chain of carbon atoms or may interrupt a chain of carbon atoms. Examples of side chain substituents are ether groups e.g. of formula  $OR^5$  and thioether groups of formula  $SR^5$ , or corresponding sulfoxides or sulphones, or secondary amine groups e.g. of formula  $NR^5R^6$ , wherein  $R^5$  and  $R^6$  are as defined below. Preferably the polar atom  
 30 interrupts a chain of carbon atoms, so that the organic monohydroxy  
 35



compound is preferably of formula  $\text{HOR}^4\text{XR}^5$ , wherein X is O, S,  $-\text{SO}_2$  or  $\text{NR}^6$ , wherein  $\text{R}^4$  represents a divalent organic group, in particular a hydrocarbyl group such as one of 1-20 carbons, as in an alkylene group e.g. of 1-6 carbons, a cycloalkylene group e.g. of 5-7 carbons, an arylene group e.g. of 6-12 carbons, or an aralkylene or aryl bis alkylene group e.g. of 7-12 or 8-12 carbons respectively, each of  $\text{R}^5$  and  $\text{R}^6$ , which may be the same or different, represents an organic hydrocarbyl group e.g. of 1-20 carbons such as alkyl e.g. of 1-6 carbons, a cycloalkyl group of 5-7 carbons, an aryl group e.g. of 6-12 carbons or an aralkyl group of 7-12 carbons. Examples of  $\text{R}^4$  are methylene, 1,2-ethylene (which are preferred) 1,3-propylene and 1,4-butylene or 1,4-cyclohexylene, or 1,2 or 1,3 or 1,4-phenylene, or 1,4-benzylene or 1,4-phenyl bis methylene (xylylene). Examples of  $\text{R}^5$  and  $\text{R}^6$  are methyl, ethyl, isopropyl or butyl, cyclohexyl, cyclopentyl phenyl, tolyl, xylyl or benzyl, but preferably methyl, ethyl or isopropyl in particular for  $\text{R}^6$  and especially for both  $\text{R}^5$  and  $\text{R}^6$ . Thus preferably the  $-\text{R}^4\text{XR}^5$  group in the monohydroxy compound is 2-methoxy ethyl and 2-methylthio ethyl, 2-ethylthio ethyl, 2,2-dimethyl amino-ethyl, and 2-p dimethylamino phenyl-ethyl.

The monohydroxy organic compound may also contain a hetero ring, preferably of 5, 6 or 7 ring atoms, and be of formula  $\text{HO}(\text{R}^7)_a(\text{R}^8)_b\text{X}^1\text{R}^9$  wherein  $\text{X}^1$  is O, S, SO or  $\text{SO}_2$  or  $\text{NR}^{10}$ , and each of a and b, which may be the same or different, is 0 or 1, and  $\text{R}^7$  is as defined above for  $\text{R}^4$ ,  $\text{R}^8$  may be as defined for  $\text{R}^4$  or, with  $\text{R}^9$  may form a trivalent group, which with the oxygen S, SO or  $\text{SO}_2$  or  $\text{NR}^{10}$  forms a heterocyclic group, optionally with the ring carbon atoms interrupted with O and/or  $\text{NR}^{10}$ ,  $\text{R}^9$  forms the trivalent group above with  $\text{R}^8$  or with  $\text{R}^{10}$  may form a divalent group which with the N atom to which they are bonded may form a heterocyclic group, optionally with the ring carbon atoms interrupted by O or  $\text{NR}^{10}$  (especially when  $\text{R}^{10}$  is as defined for  $\text{R}^6$ ), and  $\text{R}^{10}$  may be as defined for  $\text{R}^6$  or as defined above in a ring group with  $\text{R}^9$  or may with  $\text{R}^8$  or  $\text{R}^9$  form an N heterocyclic ring group. Each of  $\text{R}^8$ ,  $\text{R}^9$  and  $\text{R}^{10}$  when part of a ring can contain 1-5 carbons, subject to the ring containing 5-7 ring atoms.

Thus in the hetero ring containing compounds, when a is 1 and b is O, the  $\text{R}^7$  group can be bonded directly onto the N atom of the ring formed with  $\text{NR}^9\text{R}^{10}$  as in N(2hydroxy methyl or 2 hydroxy ethyl) piperidine. When both a and b are O, the hydroxyl group can be bonded directly to the said ring N atom as in N-hydroxy piperidine. When a is O or 1 and b is 1,  $\text{R}^8$  may form with  $\text{R}^9$  and  $\text{NR}^{10}$  or the oxygen atom a hetero ring as in hydroxy N-methyl piperidine or hydroxy methyl

tetra hydrofuran or hydroxy methyl pyridine.

The ring heterocyclic ring formed with  $R^8R^9$  and O or  $NR^{10}$ , or with  $R^9NR^{10}$  may be saturated or unsaturated, partly or fully (as in an N hetero aromatic ring) and may contain 1 nitrogen or oxygen atom and optionally 1 additional N and/or O atom. There may be 1 or more hetero rings e.g. 2 hetero ring fused or fused to each other, or 1 hetero ring and at least one carbocyclic ring, saturated or unsaturated fused or unfused to the hetero ring. The ring groups can contain 3-12 carbons and 1-3 nitrogens. Examples of the rings are pyridine, piperidine, morpholine, tetrahydrofuran pyran rings, isoquinoline and quinoline.

Examples of the organic monohydroxy compound with hetero-ring polar group are 2, 3 or 4 (2 hydroxy ethyl) tetrahydropyrrole or morpholine, 2, 3 or 4 hydroxyl N methyl piperidine and 2 hydroxyethyl or hydroxymethyl substituted in a tetrahydropyran or tetrahydrofuran ring, especially with the substituent in a 2 position.

In the copolymers may also be structural units from at least one monomer C, which is an ethylenically unsaturated carboxylic amide ( $C^1$ ). The amide is derived from an ethylenically unsaturated carboxylic acid, which may be as described with respect to monomer  $A^1$ , and ammonia or a primary or secondary amine. The amine may be of formula  $HNR^{20}R^{21}$ , where each of  $R^{20}$  and  $R^{21}$ , which may be the same or different represents an organic group or hydrogen, preferably one representing hydrogen, or  $R^{20}$  and  $R^{21}$  together with the N atom to which they are attached may form a heterocyclic ring.

Examples of the organic group are hydrocarbyl groups, such as are defined for  $R^5$  or  $R^6$  above, or hydrocarbyl groups containing at least one polar group, for which the nature and location of polar groups may be as described above in respect of monomer  $B^1$ . Advantageously the amine containing the hydrocarbyl group and a polar group is of formula  $H_2NR^{22}X^2R^{23}$ , wherein  $X^2$  is O, S or  $NR^{27}$ ,  $R^{22}$ ,  $R^{23}$  and  $R^{27}$  are as defined for  $R^4$ ,  $R^5$  and  $R^6$  respectively, or of formula  $H_2N(R^{24})_c(R^{25})_dX^2R^{26}$ , wherein c is 0 or 1, d is 0 or 1  $X^2$  is O, S or  $NR^{10}$  and  $R^{24}$ ,  $R^{25}$  and  $R^{26}$  are as respectively defined for  $R^7$ ,  $R^8$  and  $R^9$  above.

Thus for amines for use in monomer  $C^1$ , which are hydrocarbyl amines  $R^{20}$  is preferably hydrogen while  $R^{21}$  is preferably a long or short chain alkyl or alkenyl group, e.g. respectively of 14-40, or 1-13 e.g. 1-6 carbons e.g. methyl or ethyl.  $R^{21}$  is preferably a long chain group of 16-24 carbons, in particular dodecyl, stearyl, palmityl, oleyl or octadecyl. Examples of such amines are ethylamine,

dodecylamine, stearyl amine and oleyl amine. Benzylamine may also be used.

For amines in which  $R^{20}$  and  $R^{21}$  together with the N atom to which they are attached form a heterocyclic ring, the ring usually contains 5, 6 or 7, especially 6 ring atoms, with 1 nitrogen atom. The ring may be saturated or partly

5 ethylenically unsaturated and may be unsubstituted or substituted by one or more alkyl groups e.g. of 1-6 carbons, such as methyl or ethyl. Examples of such amines are piperidine and tetrahydropyrrole and their ring methyl derivatives.

Preferably the amine contains an additional polar group as described above. The additional polar group may be a N or O atom not bonded in a ring or part of a

10 ring. Preferably the N atom is not part of a ring, so the amine is of formula  $H_2NR^{22}NR^{23}R^6$ , wherein  $R^{22}$ ,  $R^{23}$  and  $R^6$  are defined above;  $R^{22}$  is especially alkylene of 1-4 carbons e.g. methylene or 1,2-ethylene, while  $R^{23}$  and  $R^6$  are especially alkyl of 1-6 carbons, such as methyl ethyl or isopropyl. Thus the amine may be 2(dimethylamino)ethylamine or 2-(diethylamino)ethylamine. The amine

15 may also contain an oxygen atom not in a ring such as one of formula  $H_2NR^{22}OR^{23}$  wherein  $R^{22}$  and  $R^{23}$  are as defined above, in particular  $R^{22}$  being alkylene of 1-4 carbons e.g. methylene or 1,2 ethylene, and  $R^{23}$  being especially alkyl of 1-6 carbons such as methyl, ethyl or isopropyl. Examples of such amines are 2-butoxyethylamine and 2-ethoxyethylamine. The amine may also contain an oxygen

20 atom in a ring e.g. be of formula  $H_2N(R^{24})_c(R^{25})_dOR^{26}$ , wherein  $R^{24}$  is as defined for  $R^7$ , and is especially methylene or 1,2-ethylene, and  $R^{25}$  and  $R^{26}$  and the O atom form a heterocyclic ring in the way  $R^8$  and  $R^9$  and the oxygen atom above form such a ring. Examples of such rings are tetrahydrofuran, and tetrahydropyran rings. Examples of such amines are 2-aminomethyl-tetrahydrofuran and -

25 tetrahydropyran. N heterocyclic ring substituted alkyl amines may also be used, in particular the amino analogues of the alcohols with a hetero cyclic ring described above with the OH group replaced by an  $NH_2$  group. Examples of these are aminomethyl- and 2 amino ethyl-pyridines and piperidines and morpholines.

In the copolymers may be structural units  $A^{11}$  from at least one ester of an

30 ethylenically unsaturated alcohol, and/or said alcohol itself, including mixtures of alcohol and ester units e.g. with 1-50% alcohol with 99-50% ester or 99-50% alcohol and 1-50% ester. The structural unit  $A^{11}$  may consist essentially of said alcohol or said ester or both. The ethylenically unsaturated alcohol may contain the unsaturated group, alpha, beta or gamma to the alcohol group or in another

35 location. It may contain 2-6 carbons, and is preferably allyl alcohol, methallyl

alcohol, alpha methyl vinyl alcohol or especially "vinyl alcohol" ( $\text{CH}_2=\text{CHOH}$ ), which can form structural units for the ester polymers.

The carboxylic acid for use in the structural units with such unsaturated alcohols may be an alkanoic acid e.g. of 1-24 carbons, such as 1-5 carbons, especially for alkanoic acids such as formic acetic, propionic and butyric acids, 3-24 carbon alkenoic acid e.g. oleic acid or 6-24 carbon alkanoic acids, in particular ones which are linear or have at least one methyl or ethyl branch. The carboxylic acid may have a larger organic hydrocarbyl group, such as one of 6-24 carbons, e.g. an alkanoic acid of 6-16 carbons such as hexanoic, octanoic, 2 ethyl hexanoic, isooctanoic, decanoic, lauric, dodecanoic, myristic or palmitic, or a cycloalkanoic e.g. of 6-8 carbons such as cyclohexanoic acid, or aromatic hydrocarbyl carboxylic e.g. of 7-14 carbons such as benzoic or toluic, or aralkanoic acid e.g. of 8-15 carbons such as 2-phenyl ethanoic acid. The acid may contain 14-40 carbons such as 15-25 carbons, especially 16, 18, 20, 22 or 24 carbons. The acid may be natural or synthetic e.g. derived from oxo or ALFOL process alcohols. Examples of suitable acids are oleic, palmitic, hexadecanoic, stearic, octadecanoic, and eicosanoic. The saturated or unsaturated acids may be substantially pure, but are preferably mixtures of acids, e.g. as in tallow acid or mixtures of acids of even carbon number with one carbon number predominating with decreasing proportions or acids of lower and higher carbon number (e.g. of Gaussian distribution) i.e. with carbon numbers distributed on either side of the major one. Such mixtures may contain at least 50% e.g. at least 80 or 90% (by mole) of one alkanoic or alkenoic acid and smaller amount(s) of other alkanoic or alkenoic acid(s). Examples of such mixtures are unsaturated acids e.g. of 16 or 18 carbons containing (in wt%) 50-100% cis-acid, (such as in commercial oleic acid) or saturated acids e.g. behenic acid with a majority of 22 carbon alkanoic acid and smaller amounts of 16, 18, 20 and 24 carbon alkanoic acids.

Preferably the monomer  $A^{11}$  is an ester of an unsaturated alcohol with 3-6 carbons and a saturated carboxylic acid of 2-5 or 6-24 carbons. Especially preferred are esters of "vinyl alcohol" and acetic or propionic acids.

Thus monomer  $A^{11}$  may be of formula



wherein each of  $\text{R}^{30}$  and  $\text{R}^{31}$ , which may be the same or different may be as defined for  $\text{R}^1$  or  $\text{R}^2$ , while  $\text{R}^{32}$  may be as defined for  $\text{R}^3$ , especially where  $\text{R}^3\text{CO}_2\text{H}$

represents the carboxylic acid which is an alkanoic acid of 1-6 carbons or one with

a larger organic hydrocarbonyl group as described above or a mixture thereof in particular ones in which the molar ratio of short to larger e.g. long chain acid groups for  $R^3$  is as described above. Preferably  $R^1$  and  $R^2$  are hydrogen and  $R^3$  is alkyl e.g. 1-5 or 6-24 carbons. The monomer  $A^{11}$  may also be of formula

5  $R^{33}OCR^{30}=CHR^{31}$ , where  $R^{33}$  is hydrogen or  $R^{32}CO$ .

A mixture of monomer units from unsaturated alcohols may be present, in particular when  $R^{33}$  is hydrogen, and when  $R^{33}$  is  $R^{32}CO$ , especially in molar ratios of 0.5-99.5 : 99.5-0.5, in particular 1-99:99-1, 5-95:95-5 or 10-50:90-50 or 90-50 : 10-50 e.g. 10-40 : 90-60, 5 - 40: 95 - 60, 90-60 : 10-40, or 95 - 60: 5 - 40.

10 Increasing the proportion of  $R^{32}CO$  groups increases the hydrocarbon solubility and molecular weight of the polymer. Mixtures of units from alcohols with short and long chain groups for  $R^{33}$  may have the proportions for  $R^3$  as defined for  $R^3$  above. Preferred are polymers from structural units of vinyl alcohol and vinyl acetate, laurate, and/or palmitate. Most preferred are polymers whose structural

15 units  $A^{11}$  consist essentially of "vinyl" alcohol, and vinyl alcohol with vinyl acetate, laurate, palmitate, especially with the esters in molar amounts of 1 to 20% total monomer units for  $A^{11}$ .

In the copolymers from unsaturated alcohols for  $A^{11}$ , may also be structural units from at least one monomer  $B^{11}$  which is an ester of an ethylenically

20 unsaturated alcohol and an organic mono carboxylic acid with at least one additional polar group. The alcohol may be as described with respect to monomer  $A^{11}$ . The additional polar group may contain an oxygen, nitrogen or sulphur atom, especially one or more O and/or N atoms. The or each polar group may be a side chain substituent on a chain of carbon atoms or may interrupt a chain of carbon

25 atoms. Examples of side chain substituents are other groups e.g. of formula  $RO^5$  or secondary amine groups e.g. of formula  $NR^5R^6$ , wherein  $R^5$  and  $R^6$  are as defined above. Preferably the polar atom interrupts a chain of carbon atoms, so that the organic carboxylic acid is preferably of formula  $HOOCR^4XR^5$ , wherein X,  $R^4$ ,  $R^5$  are as defined and exemplified above.

30 Preferably the  $-R^4XR^5$  group in the carboxylic acid compound is methoxy phenyl, methoxy methyl, 2-methoxy ethyl and methylthio methyl, 2-methylthio ethyl or 3-methylthio propyl, methylthio phenyl-, 2-phenylthio ethyl-, 2,2-dimethyl amino-ethyl, 2-dimethylamino phenyl-ethyl (especially with the dimethylamino group in o or p position, dimethylamino methyl and dimethyl amino phenyl.

35 The organic carboxylic acid may also contain a hetero ring, preferably of 5,

6 or 7 ring atoms, and be of formula  $\text{HOOC}(\text{R}^7)_a(\text{R}^8)_b\text{X}^1\text{R}^9$  wherein  $\text{R}^7$ ,  $\text{R}^8$ ,  $\text{R}^9$ ,  $\text{X}^1$  are as defined and described above.

Thus in the hetero ring containing compounds, when a is 1 and b is O, the  $\text{R}^7$  group can be bonded directly onto the N atom of the ring formed with  $\text{NR}^9\text{R}^{10}$  as in N(carboxy methyl) piperidine. When a is O or 1 and b is 1,  $\text{R}^8$  may form with  $\text{R}^9$  and  $\text{NR}^{10}$  or the oxygen atom a hetero ring as in N-methyl piperidine carboxylic acid or tetra hydrofuran carboxylic acid or pyridine carboxylic acid or picolinic acid.

The ring heterocyclic ring formed with  $\text{R}^8\text{R}^9$  and O or  $\text{NR}^{10}$ , or with  $\text{N}^9\text{NR}^{10}$  may be saturated or unsaturated, partly or fully (as in an N hetero aromatic ring) and may contain 1 nitrogen or oxygen atom and optionally 1 additional N and/or O atom. There may be 1 or more hetero rings e.g. 2 hetero ring fused or infused to each other, or 1 hetero ring and carbocyclic ring, saturated or unsaturated fused or unfused to the hetero ring. The ring groups can contain 3-12 carbons and 1-3 nitrogens. Examples of the rings are pyridine, piperidine, morpholine, tetrahydrofuran pyran rings, isoquinoline and quinoline.

Examples of the organic monocarboxy compound with hetero-ring polar group are 2,3 or 4 (carboxymethyl) tetrahydropyrrole or morpholine, N methyl piperidine carboxylic acid and carboxymethyl or carboxy substituted in a tetra hydropyran or tetra hydrofuran ring, especially with the substituent in a 2 position.

The copolymer may have structural units from monomers A and B (including  $\text{A}^1\text{B}^1$  or  $\text{A}^{11}\text{B}^{11}$ ), in which case the molar percentages may be 30-95%B, e.g. 40-80% such as 50-70%B (especially when  $\text{B}^1$  is derived from a nitrogenous alcohol) or 60-80% (especially when  $\text{B}^1$  is derived from an ether alcohol), with 70-5%A, e.g. 60-20%A or 50-30%A or 40-20%A; the copolymer especially consists essentially of structural units of such monomers. In the oil-soluble embodiments of the invention, the copolymer may comprise 1 -95 molar % B, preferably 1 to 80%, more preferably, 1 to 10%, and most preferably, 1 to 5% B. The copolymers may contain at least 10.1% by weight of structural units from B, e.g. 11-80 such as 35-60wt% in particular in copolymers of A and B, especially when monomers  $\text{A}^1$  comprise both long and short chain aliphatic alcohol groups e.g. from  $\text{R}^3\text{OH}$  in particular ones with at least 30% of long chain groups, based on the total of said aliphatic groups. The copolymers may contain (a) 1 - 99%, for example, 80 - 99%, 10-70% or 20-50% of short chain monomer A units (including  $\text{A}^1$ ,  $\text{A}^{11}$ ) (e.g. alkyl(meth)acrylate or vinyl alkanoate esters with 1-4 carbons in the alkyl or

alkanoate group), (b) 0 - 99%, 0-60% e.g. 0 or 10-60% e.g. 20-40% of larger monomer A units (including A<sup>1</sup>, A<sup>11</sup>) (e.g. alkyl(meth)acrylate or vinyl alkanoate esters with 6-18 e.g. 6-12 carbons in the alkyl or alkanoate group) and (c) 5-50% e.g. 10-30% of structural units from monomer B (including B<sup>1</sup> B<sup>11</sup>), in particular one in which the polar group is 1 or 2 amine or ether groups. The molar proportions of the units (a):(b):(c) are usually 0.5-4 (e.g. 0.5-3): 0.5-1.5 (e.g. 0.8-1.3 especially 1) : 0.5-1.5 (e.g. 0.8-1.3 especially 1). The copolymer may have structural units from monomers A and C including A<sup>1</sup> C in which case the molar percentages may be 0 - 99% C, for example, 0 - 10% C, or 5-80%C. For instance, the copolymer may be 5-50%C or 8-25C or 20-45%C and 95-20%A, e.g. 95-50%, or 92-75% or 80-55%A, the copolymer especially consisting essentially of structural units of such monomers. The copolymers may also contain units from monomers A, B and C (including A<sup>1</sup>, A<sup>11</sup>, B<sup>1</sup>, B<sup>11</sup> C<sup>1</sup>) in which case the molar percentages may be 1 - 80% B, for example, 1 to 10% B. The copolymer may also be 5-60%B, e.g. 20-50%B, 5-50%C e.g. 8-25%C, and have preferred total of B and C of 20-95% e.g. 40-80% or 50-70%, and a molar percentage of A of 5-80% e.g. 60-20% or 50-30%, the copolymer especially consisting essentially of structural units of such monomers). The units of monomer A may be from ester monomers, but are especially from acid or both acid and ester monomers and the above percentages apply to the amounts of ester monomer as sole A unit, or acid monomer as sole A unit or the total of both. Preferred are copolymers with an ester monomer units for A, and basic N containing monomers for B and/or C (i.e. copolymers D) or copolymers with a carboxylic acid units for A, and non basic N containing monomers B and/or C (i.e. copolymers E), or carboxylic acid for A with basic N containing monomers for B and/or C which are zwitterions.

The copolymers may be made by direct copolymerisation of the monomer units, A, especially when it only contains ester groups and not carboxylic acid ones, and B and/or C, especially when the monomer is free of any NH group. In the direct copolymerization, the monomers are usually all present from the start, though partial or complete polymerization of some monomer(s) e.g. A, followed by addition of monomer e.g. B, and optionally A, as in graft polymerization may be performed. Preferably however, the polymers by direct polymerization are random not graft or block copolymers. Preferably monomers of type A<sup>+</sup>, B<sup>1</sup> and/or C<sup>1</sup> react together, or of type A<sup>11</sup> and B<sup>11</sup>, though ones of A<sup>1</sup> and B<sup>11</sup> or A<sup>11</sup> and B<sup>1</sup> can be reacted.

The copolymerisation may be performed in a conventional manner e.g. with or without a diluent e.g. a hydrocarbon solvent, such as hexane, heptane, or a higher boiling hydrocarbon oil, at a temperature of 25-120°C, such as 60-100°C, and optionally in the presence of a free radical catalyst, such as a peroxide (e.g. benzoyl peroxide) or azo catalyst such as azobis isobutyronitrile. The polymerisation is usually performed under inert conditions e.g. under nitrogen or argon. The polymerisation time may be 0.5-40hr, preferably 5-25hr at 60-100°C. At the end of the polymerisation, the reaction product may be purified by evaporation under vacuum to remove unreacted monomer, and/or precipitation of the product with methanol from a liquid aromatic or aliphatic hydrocarbon solution of the product.

Preferably however, the copolymers A + B are made by reaction of a polymer of one or more ester monomer units A (i.e. A<sup>1</sup> or A<sup>11</sup>) which are derived from an unsaturated acid (or unsaturated alcohol) and optionally an ester thereof, with an organic mono hydroxy compound (or organic carboxylic acid respectively) with at least one additional polar group, as described above, in particular one of formula HOR<sup>4</sup>XR<sup>5</sup> or HO(R<sup>7</sup>)<sub>a</sub>(R<sup>8</sup>)<sub>b</sub>XR<sup>9</sup> (or HO<sub>2</sub>CR<sup>4</sup>XR<sup>5</sup> or HO<sub>2</sub>C(R<sup>7</sup>)<sub>a</sub>(R<sup>8</sup>)<sub>b</sub>X<sup>1</sup>R<sup>9</sup> respectively). Instead of either of the latter carboxylic acids a corresponding lower alkyl (C<sub>1-4</sub>) ester (e.g. methyl, ethyl propyl tertbutyl ester may be used. The reaction product may contain at least 50% of structural units for A with carboxylic acid (or alcohol) groups, or may contain less than this, including substantially no units A with acid or alcohol group, e.g. only ester groups. Optionally in the former case, and essentially in the latter case at least some ester groups for A in the reaction product are converted into polymers with at least 50% of the corresponding acid or hydroxylic groups usually by hydrolysis, but optionally by hydrogenolysis in the case of benzyl esters.

Preferably copolymers A<sup>1</sup> + C<sup>1</sup> derived from an unsaturated acid are made by reaction of a polymer of one or more corresponding monomer units A<sup>1</sup>, which are acid A<sup>1</sup>, an ester thereof or both, with ammonia, or a primary or secondary amine, in particular one of formula HNR<sup>20</sup>R<sup>21</sup> or H<sub>2</sub>NR<sup>22</sup>X<sup>2</sup>R<sup>23</sup> or H<sub>2</sub>N(R<sup>24</sup>)<sub>c</sub>(R<sup>25</sup>)<sub>d</sub>X<sup>2</sup>R<sup>26</sup>. As with copolymers A + B, the reaction product may be treated if desired or necessary to reduce its ester content for A.

The reaction may be performed in the absence of but preferably in the presence of a liquid aromatic or aliphatic hydrocarbon solvent, by reaction of an ester hydroxyl, acid, acid ester or hydroxy ester polymer from monomer A,



- especially an ester with 1-4 carbons in the alcohol (or acid) group with the organic monohydroxy compound (or carboxylic acid) having the polar group, or ammonia or said amine in the case of unsaturated acid polymers. The reaction may be performed with an amount of the said compound or ammonia or amine
- 5 substantially corresponding to the amount needed for the degree of conversion required, or an amount in excess of this e.g. substantially corresponding to an equimolar amount (based on the units of monomer ester A in the starting polymer) may be used and the reaction stopped when the desired degree of reaction has
- 10 occurred e.g. as found from the amount of distilled by product lower alcohol or carboxylic acid or ester thereof e.g. methyl acetate. The reaction may be performed at 50-180°C e.g. 60-120°C or 100-160°C for 1-30 e.g. 5-20 hours, in the absence or presence of a catalyst e.g. an organic soluble strong acid such as an aromatic sulphonic acid e.g. p-toluene sulphonic acid or a basic catalyst, such as an alkali metal alkoxide e.g. sodium methoxide or ethoxide (added as such or
- 15 prepared in situ from alkali metal and by product lower alkanol) or a polyvalent metal alkoxide such as tetra methyl, tetra ethyl or tetraisopropyl titanate. Amounts of the catalyst e.g. basic ones such as alkali metal alkoxide may be 0.05-5% e.g. 0.1-1% by weight of the feed polymer. Basic catalysts are preferred for the reaction of the polymer esters derived from the unsaturated acids, while acid
- 20 catalysts are preferred for the reaction of the polymeric esters derived from unsaturated alcohols. During the reaction the by product lower alcohol or lower alkyl carboxylate is preferably evaporated. At the end, any solvent is advantageously evaporated, while optionally unreacted polar mono hydroxy compound or acid or amine may be evaporated e.g. under reduced pressure. The
- 25 reaction which is transesterification may be performed substantially to completion e.g. 90-100% especially 95%-100%, with substantially no unreacted starting polymer e.g. 0-10% especially 0-5%, but advantageously the amount of reaction is 30-90% e.g. 55-75% or 70-90%.

- In the transesterification the ester polymer (or acid ester polymer) which
- 30 can be reacted with the hydroxy compound with the polar group may comprise only short chain alkyl(meth) acrylate monomer units (and/or the corresponding acid) or larger alkyl(meth) acrylate polymer units or both larger and short chain units. The last copolymers may themselves have been made by copolymerization or transesterification from the short chain alkyl polymers and larger alcohols e.g.
- 35 long chain alcohols according to the general procedure described above. In a

similar way the ester polymer or hydroxyl ester polymer to be reacted with the organic carboxylic acid (or ester) may comprise short chain alkanoate side chains, or larger organic carboxylate side chains or both. The latter may be made from the corresponding short chain alkanoate polymers and reaction with the larger acids.

- 5           The reaction of ester polymers with the amines may be performed in a similar manner to that of the polar alcohols, but in this case the reaction may be performed to the extent as described for the transesterification above but in particular 30-90% e.g. 50-80%; however preferably the reaction may be performed to 5-90% reaction, such as 5-50% such as 10-40% e.g. 10-20% or 30-50%. For  
10 certain applications, it is desirable for the extent of transesterification to be low, for example, 1 to 10%, preferably 1 to 5%.

- Copolymers of A and B and/or C, in which the structural units from monomer A contains free carboxylic groups as sole monomer A units or mixed with ester units or free hydroxyl groups may be made by cleavage of the ester link  
15 in A, e.g. by hydrolysis or hydrogenolysis (e.g. for benzyl esters) of the corresponding copolymer in which A is an ester monomer. The hydrolysis, which is usually performed in solution in an organic solvent, may be acid or base catalysed e.g. with an alkane or aromatic sulphonic acid, e.g. methane sulphonic or toluene sulphonic acid or a base such as sodium or potassium hydroxide, especially  
20 with distillation of by product alcohol from the ester. Weight amounts of the catalyst may be 0.1-5% by weight or preferably 1-10 equivalents per carboxylic ester group in monomer A in the copolymer. When carboxylic acid groups are required copolymers with ester monomers A based on lower alkyl or lower alkanoate esters are preferred as starting materials. The product free acids or acid  
25 esters may be isolated if desired by extraction into aqueous base, e.g. sodium hydroxide solution which can be separated from unreacted ester copolymers A+B and then the free acids or acid esters recovered by filtration or extraction after acidification of the aqueous solution. The product from alcohols e.g. polyvinyl alcohol derivatives may be isolated by extraction. The copolymers with free  
30 hydroxyl and/or carboxyl are of particular value for forming complexes (see below).

- The nitrogen containing polar group in the copolymers may be present in the form of a primary, secondary or tertiary amine or a quaternary salt. Quaternisation may be performed by reacting a copolymer of the invention having  
35 basic nitrogen atoms with a quaternising agent e.g. an organic halide e.g. chloride

or organic sulphate, in either of which the organic group is an alkyl group e.g. of 1-20 carbons such as methyl, ethyl, dodecyl, stearyl, alkenyl group of 3-20 carbons e.g. 3-6 such as allyl, cycloalkyl e.g. of 5-7 carbons such as cyclohexyl, aralkyl e.g. a hydrocarbyl group of 7-30 carbons such as benzyl, 2-phenyl ethyl or dodecyl benzyl. Thus a copolymer (derived from an unsaturated acid or alcohol) having ester groups from a polar amino alcohol (or amino acid) e.g. structural units from 2 dimethyl amino ethyl acrylate (or (pyridine methyl)acrylate) and e.g. methyl acrylate (and optionally larger organic acrylates) or units from vinyl 2-dimethyl (amino propionates) and e.g. vinyl acetate (and optionally a vinyl larger alkanoate, may be reacted with dimethyl or diethyl sulphate or benzylchloride, preferably with the desired proportion of quaternisation agent to basic nitrogen and in a hydrocarbon solvent. The amount of quaternisation may be such as to provide 1-20% molar of structural units with a quaternary group, e.g. 5-10%; there may also be present 0-20% molar of structural units with a basic nitrogen atom i.e. unquaternised, preferably when the total of basic nitrogen and quaternised nitrogen is 5-20%. Thus the degree of quaternisation may be partial or substantially complete. At the end of the quaternisation, any excess of quaternisation agent may be separated e.g. by evaporation, and the polymer product, if desired, isolated.

The copolymers of the invention may be crystalline but are preferably noncrystalline e.g. amorphous. Embodiments of the invention (eg the ester copolymer) may be oil soluble e.g. dissolves to an extent of at least 50ppm e.g. at least 200ppm in kerosene at 25°C. Other embodiments of the invention may be water soluble. For example, the acid or alcohol copolymers of the invention are usually water soluble e.g. to an extent at 25°C of at least 50ppm e.g. at least 200ppm at least one pH in the range 1-14, especially 2-7 or 8-13, in particular to at least 1%.

The invention also provides complexes or salts of the copolymer D, having a Lewis base in the side chain, especially ones which are nitrogenous and, in particular, ones with free hydroxyl groups in A, may be formed, with an acid which is preferably a carboxylic acid or sulphonic acid. The carboxylic acid may be an organic mono, di or tri carboxylic acid, in particular one of 1-24 carbons, e.g. an alkanolic or alkenolic acid of 1-23 carbons e.g. 2-6 or 6-18 carbons such as formic, acetic, propionic, 2-ethylhexanoic, lauric, oleic or stearic acid. Examples of the sulphonic acid are alkyl and aryl sulphonic acid, e.g. alkylsulphonic acids of 1-18 carbons such as 1-6 carbons such as methane and propane sulphonic acids, or

aromatic hydrocarbyl sulphonic acids e.g. of 6-24 carbon atoms such as benzene, toluene, xylene or dodecylbenzene sulphonic acids. The molar proportion of Lewis base e.g. basic nitrogen atoms or O or S atoms in ether groups in the copolymer e.g. in amino groups to acid groups, in the carboxylic or sulphonic acid may be 10-0.1:1 e.g. 4-0.5:1.

The above examples are of acids of molecular weight less than 1000 e.g. less than 400. But in addition polymeric acids may be used e.g. polymers with a plurality of carboxylic and/or sulphonic acid groups and optionally a Molecular weight of 400-1 million e.g. 1000-500,000 or 10,000-100,000. However, polymeric acids having higher molecular weights may also be employed, for example, polymers with molecular weights of up to 10 million, for example, 5 million, preferably, 0.5 to 5 million, and most preferably, 0.5 to 3 million. Such polymers usually have a hydrocarbon backbone and pendant acid groups, and are made by polymerisation of ethylenically unsaturated acid monomers e.g. (meth)acrylic acids. or vinyl and methyl vinyl sulphonic acids. Other polymeric carboxylic acids are polymeric carboxylic acid esters, e.g. made by copolymerising the corresponding monomers e.g. acrylic acid and alkyl acrylates, but preferably as polymeric carboxylic acid esters or acids by at least partial e.g. complete hydrolysis of copolymers of monomer A with the group  $R^3$  in the aliphatic alcohol a mixture of long and short chains, as described above. Such latter copolymers may be made by transesterification of the short chain ester polymers from A with long chain alcohol. The molecular ratio of basic N, O or S atoms in the copolymer of the invention to acid group in the polymeric acid may be 0.1-10:1 e.g. 0.5-2:1.

The invention also provides complexes or salts of copolymer E, which contain carboxylic acid groups with a base which may be inorganic or organic. Examples of inorganic bases are oxides, hydroxides, carbonates and bicarbonates of ammonia, alkali metals and alkaline earth metals, e.g. of sodium, potassium calcium or magnesium, especially sodium and potassium salts of the copolymer E. Examples of the organic bases are amines, in particular primary, secondary or tertiary amines, such as those of formula  $HNR^{20}R^{21}$  as defined above or polyamines, such as ethylene diamine, diethylene triamine and higher homologues, or hexamethylene tetramine. The above organic bases usually have a molecular weight below 1000 or below 400, but polymeric amines may also be used with molecular weights above this e.g. 400-10 million or 400 - 1 million, such as, 1000 to 5 million, 10,000 to 3 million, or 1000-500,000 or 10,000-100,000. Polymeric

amines having higher molecular weights are also suitable, for example, polymers with molecular weights of up to 5 million, preferably, from 500,000 to 5 million, and most preferably from 0.5 to 3 million. Examples of such polymeric amines are polyethylene imine and polypropylene imine. The base may also be a Lewis base, in particular an oxygen or sulphur containing compound, especially with at least one oxygen atom in an ether (or thioether) or hydroxyl (or thiol) group. Thus the base may be of molecular weight less than 1000, e.g. less than 400, or may be polymeric with molecular weight above 1000. Examples of the bases of molecular weight less than 1000 are aliphatic mono ols (or thiols), di, tri or tetra polyols (or polythiols), such as lower alkanols e.g. methanol or ethanol, or alkylene glycols, e.g. ethylene or propylene glycols, or glycerol or pentaerythritol, or glycol ethers such as alkylene glycol ethers, e.g. mono or di lower alkyl ethers of mono, di or poly alkylene glycols. Polymeric bases may also be polyalkylene glycols or ethers thereof e.g. polyethylene glycol or block or random copolymers of ethylene and propylene glycols. Other examples of polymeric bases are partially hydrolysed polyvinylacetate. The molar ratio of acidic groups in the copolymer of the invention to basic group or atoms in the base e.g. basic N, O or S atoms may be 0.1-10:1 such as 0.5-2:1. The complexes may be made by mixing the basic copolymer and carboxylic acid (or acid copolymer and base) in the desired proportions and preferably in a solution in an organic solvent such as an aromatic hydrocarbon such as benzene, toluene or a xylene followed optionally by evaporation or other isolation method, preferably under vacuum and reduced temperature e.g. less than 100°C minimise any reactions other than complex formation.

Preferably the base copolymer D forms a complex with acid copolymer E. the molar ratio of base to acid groups being 0.1-10:1 e.g. 0.5-2:1.

The monomer A<sup>11</sup> may also be derived from an ester of an ethylenically unsaturated alcohol with a carboxylic acid, and in this case the monomer B<sup>11</sup> is usually derived from the ester of an ethylenically unsaturated alcohol and carboxylic acid with at least one extra polar group. Such copolymers of A<sup>11</sup> and B<sup>11</sup> are obtained by or are obtainable by reaction e.g. transesterification of the ester of the unsaturated alcohol with the polar carboxyl i.e. acid or an ester (or acid halide) thereof. The reaction may be performed to as low as 1% completion, for example, 1 to 10% completion. Alternatively, the reaction may be performed at least 30% e.g. 30-90% completion.

The present invention also provides blends of one or more of the copolymers of the invention, e.g. solely of different polymers of the same type e.g. ester A+B or ester A+C polymers or acid A+B or acid A+C polymers, the differences lying in different molecular weights, different chain lengths for the ester or nature of the polar group in B or nature of the amide in C. Blends may contain 90-10:10-90 e.g. 30-70:70-30 proportions of the 2 copolymers.

The ester complexes of the invention are usually oil soluble e.g. dissolve in kerosene at 25°C to at least 50ppm such as at least 200ppm, while other embodiments of the invention, for instance, the acid or alcohol complexes may be water soluble e.g. to an extent at 25°C of at least 50ppm e.g. at least 200ppm at least one pH in the range 1-14, especially 2-7 or 8-13, in particular to at least 1%.

The present invention also provides a soluble concentrate of at least 10% by weight of a copolymer or complex of the invention, e.g. 10-40% such as 20-30% by weight in a solvent e.g. water (for water soluble copolymers or complexes) or an organic solvent, such as an aromatic hydrocarbon e.g. toluene or xylene or a mixture of methyl benzenes (for oil soluble copolymers or complexes). If desired the solvent may be a mixture, for example, of the aromatic hydrocarbon and a polar oxygenated solvent such as methanol ethanol or isopropanol. Alternatively, the solvent is a mixture of water and a polar oxygenated solvent such as methanol ethanol or isopropanol. The copolymer or complexes may be made as such in the desired solvent, which may be concentrated if required, but preferably they are made in any suitable solvent, that suitable solvent evaporated and/or the copolymer or complex isolated (if desired) and the above concentrate made with the specifically desired solvent or solvent mixture. A concentrate is often easier to handle for the proposed uses than pure product or a dilute solution.

However, in some cases the copolymer or complex may not dissolve in the desired solvent (eg. water or an organic solvent) to the desired extent for a concentrate. In these cases, a dispersion in the desired solvent may be made. Thus, if an organic solvent (e.g. an aromatic hydrocarbon) is the desired solvent, and the copolymer or complex is insoluble in this solvent, a dispersion in the organic solvent is made. When the copolymer or complex does not dissolve in water, a dispersion in water of the copolymer or complex may be made e.g. with at least 5% such as 5-40 or 10-30% by weight of the copolymer or complex. The dispersion may contain water as continuous medium and the copolymer or complex as such or in a solution in organic solvent (e.g. an aromatic hydrocarbon as above) as the

disperse phase. A polar organic solvent e.g. as described above may also be present. The dispersion preferably also contains a surfactant to stabilise it (e.g. in amount 0.1-5% by weight) especially one compatible with the overall nature of the copolymer, e.g. basic polymers preferably have nonionic or cationic surfactants, while acid polymers preferably have nonionic or anionic surfactants.

The polymers of the present invention may have a molecular weight of, for example, 5 - 10 million, preferably, 20,000 to 3 (or 2) million, most preferably, 20,000 to 500,000 and especially at least 30,000 or at least 40,000, such as 40,000 to 200,000. Molecular weights of 80,000 to 160,000 may also be employed, while molecular weights of 100,000 to 5 million, for example, 100,000-2 million, and preferably 200,000-500,000 are also suitable. The weight average molecular weight ( $M_w$ ) and the molecular weight distribution ( $M_w/M_n$ ) of the polymers of the present invention may be 1.2-20 e.g. 1.2-10, preferably, 1.4-2 or 2-20 e.g. 5-15. As used herein, unless otherwise specified, the term "Molecular Weight" of an ester or amide polymer produced by reaction of the corresponding precursor ester polymer and alcohol, ammonia or amine means the weight average molecular weight of the ester polymer obtained by calculation from the percentage conversion (based on spectroscopic analysis) and the molecular weight of the precursor ester or amide polymer, or the weight average molecular weight of the ester or amide polymer itself, the molecular weight being determined by gel permeation chromatography (GPC) against polystyrene standards as described in the Aldrich Chemical Company's Standard Test Method for GPC. The term Molecular weight of an acid polymer made from ester polymer e.g. by hydrolysis is likewise defined. The term "Molecular Weight" of an ester or amide polymer produced by direct polymerisation of the corresponding ester or amide means the weight average molecular weight of the ester or amide polymer determined by gel permeation chromatography (GPC) against polystyrene standards as described in the Aldrich Chemical Company's Standard Test Method for GPC. The term molecular weight of an acid polymer made by direct copolymerization is likewise defined.

The copolymers or complexes, whether in solution, concentrated dispersion form or otherwise, may be used to alleviate problems with flowing fluids, for example, aqueous fluids and/or hydrocarbons (e.g. oil, and in particular, crude oils). The problem may be that of drag, which reduces the flow rate at constant pumping energy, or requiring higher pumping energy to maintain the same flow rate. The problem may also be that of deposition of solids, especially on cooling,

when the solids are e.g. waxes or asphaltenes.

The oil whose flow characteristics are to be improved usually comprise a liquid hydrocarbon, especially a mixture of hydrocarbons of final boiling point higher than that of lubricating oils. The hydrocarbon is usually primarily aliphatic in nature, but may contain up to 50% w/w liquid aromatic compounds. The hydrocarbon may be a crude or black oil or non volatile fraction from a distillation of crude oil, such as a vacuum, atmospheric or thermal residue. Preferably the hydrocarbon is an oil field product, e.g. either a whole well product, the multiphase mixture in or from the well bore, or one at the well head after at least partial separation of gas and/or water (and may be a condensate) e.g. an oil export fraction substantially free of separate phase gas and/or water. The liquid hydrocarbon may be flowing up a well bore, or on a production platform or between platforms or from a platform to a collection or storage facility e.g. from offshore to onshore. Particularly of interest are hydrocarbons moved in pipelines under the sea under low temperature conditions e.g. in latitudes of greater than 50° N or S or in Gulf of Mexico. The hydrocarbon may contain up to 50% by weight of wax usually 0.5-30% or 1-15% especially 2-9% and the wax may contain 20-100 e.g. 20-60 or 30-60 or 40-70 carbon atoms; the hydrocarbon may contain 0.1-5% e.g. 0.2-1% of waxes of 20-60 carbons. The hydrocarbons may contain dissolved gas (e.g. with amounts of up to 10% gas) or water or water droplets e.g. with 5-40% water (e.g. as in water in oil emulsions, so called "chocolate mousse"). There may also be, in addition to the oil, gas and/or water as a physically separate phase. The hydrocarbons may in the absence of the compounds of the invention, have a wax appearance temperature (WAT) value which approximates the cloud point value of at least 0°C e.g. 0-60°C or 10-50°C, 20-45°C or 20-40°C; pour point of such hydrocarbons may be 10-50°C e.g. 20-50°C lower than the WAT value and may be -30°C to 20°C e.g. -20°C to +10°C. The polymers, blends and compositions of the invention may reduce the WAT value of the liquid hydrocarbon by at least 2°C e.g. 2-20°C such as 5-15°C, and can reduce the rate of wax deposition per unit time.

The hydrocarbon may also be a gaseous fluid e.g. a gaseous alkane of 1-4 carbons, especially one predominating in methane, with optionally ethane, propane and/or butane, mixtures of such gaseous fluids may be used e.g. natural gas. The gaseous fluid may also contain hydrocarbon liquid e.g. as droplets (as in "wet" gas) with liquid condensate. The gaseous fluid may be a gas export line substantially



free of liquid and/or oil.

The compounds may also delay the onset of wax nucleation e.g. in a hydrocarbon liquid as shown by light scattering and they may also reduce the pour point and/or modify the wax crystals or disperse the wax. In particular the compounds may reduce the weight of wax deposition either by reducing the rate of deposition and/or by reducing the temperature of onset of deposition. The reduced wax deposition may be associated with reduced wax in suspension (i.e. reduced total wax formation) or the same or an increased amount of wax in suspension (i.e. the altering distribution of wax between suspension and deposition).

10 The polymers, concentrates or dispersions may be mixed in at least a portion of the fluid to be protected, which as mentioned above, may be a hydrocarbon, an aqueous medium or a multi-phases medium comprising both hydrocarbon an aqueous components. The polymers, concentrates or dispersions may also be mixed batchwise, continually or continuously with the body of the fluid. The body of fluid is usually a moving liquid body. Preferably, the polymers, concentrates or dispersions are added to a line containing flowing fluid to be protected, upstream of a location (usually a cooler location) where drag may otherwise increase and/or, particularly, when the fluid is oil, where wax deposition may occur. If desired the polymers concentrates or dispersions may be added to a tank of the fluid before use. If the fluid is oil, this may inhibit deposition of wax. 20 The amount of polymer, whether as such or in concentrate or dispersion, added may be 10-10,000 ppm e.g. 100-5000 ppm based on the weight of oil e.g. hydrocarbon. The polymer preferably dissolves in said fluid (oil/aqueous medium/multi-phase) to an extent of at least 10ppm e.g. at least 100ppm such as 25 100-5000ppm.

A similar approach can be applied to deal with asphaltene deposition which otherwise tends to happen in crude oils containing at least 0.05% e.g. 0.1-10% of asphaltenes and cooling e.g. to less than 20° e.g. +20 to -5°, especially +10 to 0°C.

A similar approach of addition to the flowing oil prior to a locus in which drag in the oil would otherwise be increased can be applied. Drag can occur by formation of turbulent flow in relation to pipeline surfaces and results in higher power needed to move a given amount of oil or more oil for the same amount of power. Drag reduction can occur by reduction in the amount of turbulent flow, and causes improvement in flow. The amounts of polymer or complex of the invention, whether added to the oil as such or concentrate or dispersion may be as 35

described above in relation to the reduction in wax, but the temperatures of use of the polymers for drag reduction are usually above the Wax Appearance or Cloud Pt temperatures of the oils. Concentrates or undiluted polymer or complex may be used in any oil including crude oil and fuels, but dispersions in water are preferably used when the presence of the water is not a problem e.g. with wet crude oil.

The oil soluble copolymers and complexes of the invention may be mixed with oil in an oil based drilling mud. The oil is usually a hydrocarbon oil, particularly diesel. The oil based mud is an organic liquid based drilling fluid. In the drilling fluid, there is usually present at least one weighting agent (e.g. to provide a specific gravity of 1.0-2.3) which is usually insoluble such as a barite, haematite or galena and optionally at least one conventional additive, e.g. a viscosifier e.g. organophilic clay such as treated bentonite, fluid loss control agent or biocide; the polymers may be present in 0.5-3% by weight.

The copolymers and complexes, in particular the water soluble ones, may also be used to reduce drag in aqueous media of low (or zero) salt content, such as ones with not more than 5.0% total soluble salts, such as 10-500ppm, e.g. fresh, rain or river water, or 500ppm - 1.5% e.g. aquifer water or 1-5.0% e.g. sea water. These aqueous media may be used in tertiary oil recovery, e.g. as water for tertiary water injection wells. Such media may contain also 50ppm-5% oil, as dissolved and/or suspended oil, especially produced water. Formation or produced water (the aqueous product of separating water and oil in the recovery of oil from subterranean deposit) can also be treated with the copolymers or complexes to reduce drag.

The invention also provides an injectable aqueous medium comprising at least one of said copolymers or complexes and not more than 5.0% total salts (by weight).

According to a further aspect of the present invention there is provided an aqueous medium which comprises at least one copolymer (including ter and higher polymers having structural units derived from monomers which are (A) at least one ethylenically unsaturated alcohol, carboxylic acid or ester, with at least one of (B) an ethylenically unsaturated carboxylic ester with a polar group in the ester, and (C) an ethylenically unsaturated carboxylic amide. The medium usually contains at least more than 5% e.g. at least 5.1% by weight total soluble salts. The copolymers may be derived from monomers A and/or B which are ethylenically unsaturated carboxylic acids or esters thereof, or ethylenically unsaturated alcohols

or esters thereof. The copolymers, may be acid esters, acid amides, mixed esters, ester amides or acid ester amides, or alcohol esters.

The aqueous medium of the invention comprises water and usually more than 5% total soluble salts e.g. 5.1-30% or 5.5-25% such as 10-20%. The aqueous medium may be in the substantial absence of hydrocarbon oil, in particular crude oil. It may be for use in the oil industry as a drilling fluid, well control fluid or workover fluid. In the drilling fluid, there is usually present at least one weighting agent (e.g. to provide a specific gravity of 1.0-2.3 e.g. 1.4-2.1) which may be water soluble, e.g. an alkali or alkaline earth metal halide, such as potassium chloride or caesium chloride, or insoluble such as barite, haematite or galena, and optionally at least one conventional additive, e.g. a shale inhibitor such as potassium chloride (e.g. 1-15% by weight) a starch or cellulose derivative, or polyacrylamide, a viscosifier e.g. xanthan gum, fluid loss control agent such as the starch or cellulose derivative or biocide or pH control agent e.g. sodium or potassium hydroxide; the polymers may be present in 0.5-3% by weight. The aqueous medium may also contain a polar water miscible solvent, as described above, or a glycol or glycol ether, such as di or polyethylene glycol or a C<sub>1-4</sub> alkyl mono or di ether thereof or polyethylene polypropylene glycol, amounts of which may be 1-10% by weight.

The well control fluid is a high density fluid to stop escape of oil from a well, and may contain components chosen from those for drilling fluids, but preferably with a specific gravity of 1.5-2.3. The workover fluid may also contain components chosen from those for drilling fluids but is preferably substantially free of insoluble solids e.g. insoluble weighting agents.

Thus the present invention provides an aqueous drilling workover or well control fluid comprising at least one water soluble copolymer or complex as described above and at least one conventional additive for drilling, workover or well control fluids.

For drag reduction uses, if desired, and especially with dispersions the polymer may be used with at least one thickening agent e.g. a polymeric water-soluble compound such as a gum e.g. guar gum or cellulose derivative e.g. carboxymethyl cellulose. To help stabilise the dispersions for the drag reduction at least one surfactant may also be present, e.g. a cationic anionic or ampholytic surfactant but especially a nonionic one e.g. of HLB of 5-15, such as a polyoxyethylene derivative of a sorbitan mono alkanoate or alkenoate. The amount of surfactant may be 0.05-5% e.g. 0.5-2% by weight of the total weight of

dispersion.

The invention is illustrated in the following Examples.

#### Example 1

Preparation of copolymer of methylacrylate and 2-(hydroxymethyl)pyridine.

- 5 A solution of poly(methyl acrylate) in toluene (41.5% in toluene, polymer average molecular wt. 40,000)[10.36g, 50mmol] was dissolved in toluene [50ml]. 2-(Hydroxymethyl)pyridine [4.98g, 46mmol] was added and the solution heated to 70°C. Sodium methoxide in methanol (25% solution) [370ul] was added in one portion and the solution brought to reflux for 7.5h. At periodic intervals during the
- 10 reflux the distillate was removed and replaced with fresh toluene [4 x 25 ml]. The reaction product was concentrated to dryness to afford the transesterified polymer. Yield of transesterified product as a proportion of total polymer = 58% (by nmr) (i.e. 58% of the CO<sub>2</sub> CH<sub>3</sub> groups have been replaced by CO<sub>2</sub>CH<sub>2</sub> pyridyl groups.

#### Example 2

- 15 Preparation of copolymer of methylacrylate and 2-(hydroxymethyl) tetrahydropyran.

The process of Ex.1 was repeated with the hydroxymethyl pyridine replaced by tetrahydrofurfuryl alcohol [4.63g, 45mmol] and the reflux was for 6.0h. Yield of transesterified product as a proportion of total polymer was 65%

20 (by nmr).

#### Example 3

Preparation of copolymer of methylacrylate and 2-diethylaminoethanol.

- The process of Ex.1 was repeated with the hydroxymethyl pyridine replaced by 2-diethylaminoethanol [5.30g, 45mmol] and the reflux was for 7h.
- 25 Yield of transesterified product as a proportion of total polymer was 55% (by nmr).

#### Example 4

Preparation of copolymer of methyl acrylate and amide of acrylic acid and N,N-diethyl ethylenediamine.

- 30 A solution of poly(methyl acrylate) in toluene (41.5% in toluene, average molecular wt. 40,000)[2.8 g, 100mmol] was dissolved in toluene [100ml]. *NN*-Diethyl ethylenediamine [11.02 g, 95mmol] was added and the solution heated to 70°C. Sodium methoxide in methanol (25% solution 1.4 ml) was added in one portion and the solution brought to reflux for 7h. At periodic intervals during the
- 35 reflux the distillate was removed and replaced with fresh toluene [3 x 25 ml].

The reaction product was concentrated to dryness to afford the partly transamidated polymer. Degree of amidation as a proportion of total polymer 15% (by nmr), so the product copolymer has 85%  $\text{CO}_2\text{CH}_3$  groups and 15%  $\text{CONHC}_2\text{H}_4\text{NEt}_2$  groups in its side chains.

5 Example 5

Preparation of copolymer of methylacrylate and amide of acrylic acid and N,N-diethylethylenediamine.

The process of Ex.4 was repeated with a solution of poly(methyl acrylate) in toluene (41.5% in toluene, average molecular wt. 40,000)[10.40g, 50mmol]  
10 dissolved in toluene [50ml]. N,N-Diethylethylene diamine [5.85g, 50mmol] was added and the solution heated to 70°C. Titanium isopropoxide (0.37 ml) was added in one portion and the solution brought to reflux for 7h. At periodic intervals during the reflux the distillate was removed and replaced with fresh toluene [3 x 25 ml]. The reaction product was concentrated to dryness to afford  
15 the partly transamidated polymer. Degree of amidation as a proportion of total polymer 11% (by nmr).

Example 6

Preparation of copolymer of methyl acrylate and amide of acrylic acid and 2-dimethylamino-ethylamine.

20 A 2 necked round bottom flask was equipped with stirrer, condenser and solvent trap adapter half filled with 3A molecular sieves. The assembly was such that the distillation vapours were condensed on the molecular sieves before returning to the reaction vessel. The apparatus was charged with toluene [100ml], 2-dimethylaminoethylamine [3.95g] and polymethyl acrylate [10.42g] (41.5%  
25 solution in toluene average molecular weight 40K). The reaction mixture was heated to 70°C and sodium methoxide in methanol [370ul] (25% solution) was added in one portion. The mixture was then heated to reflux for 7h and allowed to cool for 8h. The solution was concentrated to dryness on a rotary evaporator to afford a thick gum. Degree of amidation as a proportion of total polymer 35% (by  
30 nmr).

Example 7

Preparation of copolymer of methylacrylate and acrylic ester of 4-(2-hydroxyethyl) morpholine.

The process of Ex.1 was repeated with a N-(2-Hydroxymethyl)  
35 morpholine [5.90g, 45mmol]. The solution was allowed to cool overnight and

concentrated to afford a thick amber gum. Yield of transesterified product as a proportion of total polymer 59% (by nmr).

#### Example 8-17

5 In a similar manner to that of Ex.1 were made the corresponding transesterified products from 4-hydroxymethyl pyridine (38% reaction), 3-hydroxymethyl pyridine (46% reaction) and 2-(2 hydroxyethyl) pyridine (23% reaction).

10 In a similar manner to that in Ex.2 were made the corresponding transesterified product from 2-hydroxymethyltetrahydropyran (71% reaction).

10 In a similar manner to that in Ex.3 were made the corresponding transesterified products from 2-dimethylamino ethanol (56% reaction) and 2-diisopropylaminoethanol (32% reaction).

15 In a similar manner to that of Ex.4 was made the ester amide from methylacrylate and the amide of acrylic acid and 2-aminomethyl tetrahydrofuran.

15 In a similar matter to that of Ex.7 were made the transesterified products from 3-hydroxy N-methyl piperidine, N-(2 hydroxy ethyl) tetrahydropyrrole and 4 hydroxy N-methyl piperidine (23% reaction).

#### Example 18

20 The copolymers of Ex.1-17 were each dissolved in toluene to give 25% concentrates.

#### Example 19 and 20

25 The copolymer of Ex.1 (3g) was dissolved in toluene 30ml and water (1ml) added. The mixture obtained was stirred for 48hr at room temperature and then the solvent evaporated under vacuum to leave a white solid, which nmr showed to contain carboxylic acid groups (from hydrolysis of the methyl ester in the copolymer) (about 6% of the total monomer units).

The process was repeated with the copolymer of Ex.2 to provide a copolymer with some carboxyl groups.

#### Example 21

30 Equimolar amounts of the basic copolymer of Ex.1 and the acidic copolymer of Ex.19 were separately dissolved in toluene and mixed with stirring to give a complex.

#### Example 22

35 The copolymers of Ex.1-20 and complex of Ex.21 in 5% solution in xylene were tested for drag reduction in the following manner.

A loop for testing drag reduction was as described in SPE 28966 the disclosure of which is incorporated by reference. A 25m loop maintained in a thermostated enclosure has an outer diameter of 1.27cm (0.5in) with 4 main parts in eight sections the first four of which are of 3.75m length and the last four of which are of 2.5m length. Crude oils of Southern England was passed round the loop at 10 l/min and the pressure drop across each section monitored before, during and after addition of the copolymer solution. The degree of reduction in the pressure drop across each section as a result of addition of the polymer compared to the drop in its absence is a measure of the effectiveness of the copolymer as a drag reducer. The copolymers and complex of Ex.1-21 show drag reducing behaviour.

#### Examples 23 to 37

The copolymer of Ex.3 (3g) was dissolved in toluene 30ml and water (1ml) added. The mixture obtained was stirred for 48hr at room temperature and then the solvent evaporated under vacuum to leave a white solid, which nmr showed to contain carboxylic acid groups (from hydrolysis of the methyl ester in the copolymer) (about 6% of the total monomer units).

The process was repeated with the copolymers of Ex. 4 to 17 to provide a copolymer with some carboxyl groups.

#### Example 38

The copolymers of Examples 19, 20 and 23 to 37 were hydrolysed, and found to be water soluble. These copolymers in water were tested for drag reduction in the following manner:

A loop for testing drag reduction was as described in SPE 28966 the disclosure of which is incorporated by reference. A 25m loop maintained in a thermostated enclosure has an outer diameter of 1.27cm (0.5in) with 4 main parts in eight sections the first four of which are of 3.75m length and the last four of which are of 2.5m length. An aqueous drilling fluid containing 15% potassium chloride (by weight) was passed round the loop at 10 l/min and the pressure drop across each section monitored before, during and after addition of the copolymer solution. The degree of reduction in the pressure drop across each section as a result of addition of the polymer compared to the drop in its absence is a measure of the effectiveness of the copolymer as a drag reducer. The copolymers of Ex.19, 20 and 23 to 37 show drag reducing behaviour.

#### Example 39

In this Example, high molecular weight poly(methyl acrylate) is transesterified. The resulting polymer is suitable for improving the flow characteristics of a fluid medium.

5 Poly(methyl acrylate) (Mw 1.6M) [4.48g, 52mmol] was placed in a 2 neck round bottom flask fitted with dean stark apparatus and condenser with dimethylaminoethanol [0.23g, 2.6mmol] and toluene [200ml]. The reaction mixture was brought to reflux for 1h. Sodium methoxide in methanol solution 25% [4 x 0.1 ml] added at 1h intervals. The reflux was allowed to continue for 8h and the solution allowed to cool. NMR showed that the material was transesterified to 10 5%.

#### Example 40

In this example, a copolymer having a molecular weight of approximately 1 million, and a copolymer having a molecular weight of approximately 5 million are prepared.

15 In a dimpled polymer kettle was placed water (hplc grade) [300 ml], methyl acrylate [100g, 1.16 mol] sodium lauryl sulfate [5.0g] and potassium persulfate [0.30g]. The solution was degassed by two freeze thaw cycles. The solution was then stirred vigorously to form an emulsion and the bath temperature raised to 50 C. After about 30 minutes the internal temperature was 80 C (ie reaction and 20 exotherm occurring). After 4h stirring was stopped and the solution was allowed to cool.

The reaction mixture was then precipitated by pouring into aluminium sulfate solution 1% [1L] and the precipitated polymer washed with two changes of water.

#### *Isolation of '1M' polymer*

25 The polymer was then dried overnight in a vacuum oven at 50 C The dried polymer was then dissolved in hot toluene [2.5L] and allowed to cool and the solution decanted from the undissolved material. The polymer was isolated by precipitation from 3x the volume of methanol. GPC showed the material to have the following characteristics. Mn 562000 Mw 1621000 Mw/Mn 2.9 Mpk 1012000

#### *Isolation of '5M' polymer*

30 The undissolved material was dissolved in ethyl acetate [3 x 1L] and precipitated by addition of each 1L of ethyl acetate solution into methanol [2.5L]. The supernatant was decanted off and the polymer isolated by centrifugation in 60ml tubes at 1000rpm. The collected polymer was then dried overnight.

35 GPC showed the material to have the following characteristics. Mn 903000 Mw



5348000 Mw/Mn 5.9 Mpk 2938000

Example 41

In this example, a polymer is sulphonated. The resulting polymer may be added to a fluid to improve its flow characteristics.

- 5 A 3 neck rb flask was fitted with overhead stirrer, condenser and thermometer and charged with polystyrene (average Mw 280K) [20.8g] and carbon tetrachloride [100ml]. The solution was then warmed to 65 C. Ethylene dichloride [100ml] and acetic anhydride [0.91ml] were added followed by sulfuring acid [0.61g] over ~30s the solution was left to stir for 1h and then quenched by the addition of methanol [50ml].
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The solution was concentrated on a rotary evaporator to dryness, and then suspended in xylene to a volume of [550 ml].

The resulting polymer was tested by nmr using the method described in Polymer 1986 volume 27. The results confirmed that sulphonation had occurred.

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## Claims:

1. A copolymer having structural units derived from monomers which are (A) at least one ethylenically unsaturated alcohol, carboxylic acid or ester, with at least one of (B) an ethylenically unsaturated carboxylic ester with a polar group in the ester, and (C) an ethylenically unsaturated carboxylic amide.
- 5 2. A copolymer as claimed in claim 1 which can be derived from monomers A and/or B, which are ethylenically unsaturated carboxylic acids or esters thereof, or esters of ethylenically unsaturated alcohols.
3. A copolymer as claimed in claim 1 or claim 2, which is an acid ester, an acid amide, mixed ester, ester amide or acid ester amide, or alcohol ester.
- 10 4. A copolymer as claimed in any preceding claim having a molecular weight of 30,000 to 10 million.
5. A method of improving the flow characteristics of a fluid, which method comprises mixing with said fluid, a copolymer as claimed in any preceding claim.
6. A method as claimed in claim 5, wherein said fluid is a hydrocarbon fluid, and aqueous fluid, and/or a mixture comprising aqueous and hydrocarbon components.
- 15 7. A method as claimed in claim 5 or 6, wherein said copolymer is mixed with said fluid in a batchwise or continuous manner.
8. A method as claimed in claim 7, wherein said fluid moves along a confined path defined by a conduit, and wherein said copolymer is mixed with said fluid by adding said copolymer to said conduit upstream of a location where wax deposition and/or drag problems would otherwise be encountered in the absence of said copolymer.
- 20 9. Use of a copolymer as claimed in any of claims 1 to 4, as a flow-improver for a fluid.
- 25

10. Use of a copolymer as claimed in any one of claims 1 to 4, as an inhibitor for inhibiting the deposition of asphaltene in a conduit containing a flowing fluid.

11. Use of a copolymer as claimed in any one of claims 1 to 4, for reducing drag in a fluid flowing through a conduit.

5 12. An aqueous medium which comprises a copolymer as claimed in any one of claims 1 to 4.

13. A medium as claimed in claim 12, which contains more than 5% by weight total soluble salts.

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# INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/GB 99/01320

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F8/12 C08F8/14 C08F8/30 C08F8/44 C10L1/22  
C10M149/06 C10M149/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C10L C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 892 816 A (W. LOWE) 30 June 1959 (1959-06-30) column 4, line 30 - column 5, line 39 column 8, line 27 - column 10, line 11 column 11, line 36 - column 12, line 67; claims 1-8	1-13
X	FR 1 167 856 A (N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ) 2 December 1958 (1958-12-02) the whole document	1-13
Y	FR 2 374 338 A (MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 13 July 1978 (1978-07-13) page 9, line 11 - line 31 page 20, line 18 - line 24; claims 1-6	1-13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

13 August 1999

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# INTERNATIONAL SEARCH REPORT

Inte. onal Application No

PCT/GB 99/01320

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 613 910 A (TH. GOLDSCHMIDT AG) 7 September 1994 (1994-09-07) page 2, line 29 - page 8, line 11; claims 1-11 ---	1-13
Y	EP 0 447 785 A (TH. GOLDSCHMIDT AG) 25 September 1991 (1991-09-25) claims 1-7 ---	1-13
Y	US 3 637 610 A (N. JACOBSON) 25 January 1972 (1972-01-25) column 3, line 59 - column 4, line 58 column 5, line 44 - column 6, line 19 column 6, line 72 - column 7, line 43; claims 1-13 ---	1-13
A	US 5 721 200 A (S. M. SHIRODKAR) 24 February 1998 (1998-02-24) claims 1-21 ---	1
A	FR 1 276 655 A (ESSO RESEARCH AND ENGINEERING COMPANY) 16 October 1961 (1961-10-16) the whole document ---	1
A	EP 0 493 846 A (MINISTERO DELL' UNIVERSITA' E DELLA RICERCA SCIENTIFICA E TECNOLOGICA) 8 July 1992 (1992-07-08) claims 1-14 ---	1
A	EP 0 038 573 A (CHEMISCHE FABRIK STOCKHAUSEN GMBH) 28 October 1981 (1981-10-28) claims 1-6 ---	1
A	GB 989 050 A (DU PONT DE NEMOURS AND COMPANY) 14 April 1965 (1965-04-14) claims 1-7 ---	1
A	EP 0 355 408 A (BASF LACKE + FARBEN AG) 28 February 1990 (1990-02-28) page 3, line 9 - page 4, line 29 page 5, line 58 - page 6, line 19; claims 1-12 ---	1
A	FR 2 528 051 A (INSTITUT FRANCAIS DU PETROLE ET ELF FRANCE) 9 December 1983 (1983-12-09) claims 1-14 -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/01320

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2892816 A	30-06-1959	NONE	
FR 1167856 A	02-12-1958	BE 553025 A DE 1050111 B GB 816306 A NL 101833 C NL 212557 A US 2982628 A	02-05-1961
FR 2374338 A	13-07-1978	JP 54043290 A JP 1086167 C JP 53074588 A JP 56029886 B DE 2755490 A GB 1575459 A IT 1089639 B US 4144388 A	05-04-1979 26-02-1982 03-07-1978 11-07-1981 15-06-1978 24-09-1980 18-06-1985 13-03-1979
EP 613910 A	07-09-1994	DE 4306537 A DE 59400529 D JP 6298865 A US 5583184 A US 5571872 A US 5633325 A	08-09-1994 02-10-1996 25-10-1994 10-12-1996 05-11-1996 27-05-1997
EP 447785 A	25-09-1991	DE 4008761 A DE 59102534 D ES 2058946 T JP 7103182 B JP 7118341 A US 5145914 A	26-09-1991 22-09-1994 01-11-1994 08-11-1995 09-05-1995 08-09-1992
US 3637610 A	25-01-1972	NONE	
US 5721200 A	24-02-1998	US 5474694 A	12-12-1995
FR 1276655 A	16-03-1962	NONE	
EP 493846 A	08-07-1992	IT 1244474 B AT 101874 T AU 648844 B AU 8881891 A CA 2057492 A CN 1066678 A CN 1099790 A CN 1107882 A DE 69101238 D DE 69101238 T DK 493846 T ES 2049522 T HU 213734 B JP 6122864 A MX 9102506 A PL 167974 B PT 99796 A, B US 5322632 A	15-07-1994 15-03-1994 05-05-1994 18-06-1992 15-06-1992 02-12-1992 08-03-1995 06-09-1995 31-03-1994 01-06-1994 30-05-1994 16-04-1994 29-09-1997 06-05-1994 01-06-1992 30-12-1995 30-04-1993 21-06-1994
EP 38573 A	28-10-1981	DE 2856383 A	03-07-1980

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/01320

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 38573 A		DE 2911642 A	25-09-1980
		AT 15652 T	15-10-1985
		AT 15377 T	15-09-1985
		BR 7908569 A	16-09-1980
		CA 1129883 A	17-08-1982
		CA 1176797 A	23-10-1984
		CS 223886 B	25-11-1983
		CS 223883 B	25-11-1983
		DD 148213 A	13-05-1981
		DD 158244 A	05-01-1983
		EP 0013416 A	23-07-1980
		IN 153678 A	04-08-1984
		IN 160880 A	08-08-1987
		JP 1507726 C	26-07-1989
		JP 55115857 A	06-09-1980
		JP 63060732 B	25-11-1988
		RO 79816 A	01-02-1983
		US 4408073 A	04-10-1983
		US 4528350 A	09-07-1985
GB 989050 A		BE 640121 A	19-05-1964
		FR 1374082 A	13-01-1965
		NL 300642 A	
EP 355408 A	28-02-1990	DE 3827587 A	01-03-1990
		AT 81658 T	15-11-1992
		CA 1329302 A	03-05-1994
		WO 9001502 A	22-02-1990
		EP 0428553 A	29-05-1991
		ES 2052830 T	16-07-1994
		US 5229467 A	20-07-1993
FR 2528051 A	09-12-1983	DE 3320720 A	08-12-1983
		GB 2121808 A, B	04-01-1984
		IT 1185501 B	12-11-1987
		NL 8302012 A, B,	02-01-1984

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